large when the bond to water is formed. This interpretation of the data is however by no means unique, for, if the water attacked at a coordination site remote from the leaving group, only a small difference between different leaving groups would be expected. A specific effect of Ag^+ is to be noted also for the present series of experiments: NO_3^- is peculiarly efficient as an entering group in the Ag^+-assisted removal of Br^- and furthermore becomes relatively more efficient as its concentration increases. This may be a consequence of some surface effect (AgBr is formed and the reaction may take place at the surface), but the general behavior has precedent also in homogeneous solution—*cf.* the formation[3] of $Co(NH_3)_5SO_4^+$ in the Hg^{2+}-assisted removal of Cl^- from $Co(NH_3)_5Cl^{2+}$.

Before we undertook the present work, it seemed possible that the agreement in values of competition rates recorded by Haim and Taube[1] was a consequence of the fact that neutral leaving groups were involved in the reactions which they investigated. The present results obtained with $(CH_3O)_3PO$ as leaving group show that the subject is more complicated—as it is in fact expected to be if the incoming groups make bonds before the leaving group has left the scene of reaction. At the present time, the data are too sparse to reveal a pattern in the way the leaving group influences the competition between entering groups. At one extreme, when N_2 or CO_2 is the leaving group, a genuine intermediate may be formed, and in this extreme the leaving group will not influence the product composition. In the other, when a poor leaving group such as NCS^- is in question, its effect may be profound. Data for the systems involving poor leaving groups will however be hard to obtain because the replacement of the group may be slow compared to the rate at which the immediate products reequilibrate. In the intermediate range of leaving group tenacity, there are a variety of systems which can be studied, among them those in which sulfolane, alcohols, or other moderately good leaving groups are used.[20] Further experiments in this direction are planned.

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[20] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

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Relative Bond Dissociation Energies and Heats of Formation of Two Series of Five-Coordinated Metal Complexes from Manganese(II) to Zinc(II). A Calorimetric Study

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The enthalpy changes for the formation of five-coordinated high-spin complexes have been obtained. The compounds are of the type $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$—where M = Mn, Fe, Co, Ni, Cu, Zn; $Me_6tren = N[CH_2CH_2N(CH_3)_2]_3$ and $Me_5dien = CH_3N[CH_2CH_2N(CH_3)_2]_2$. Measurements of heats of solution have been made on the simple metal bromides, ligands, and complexes in hydrochloric acid and on the ligands in water. Using these data, the enthalpy changes relative to that of the manganese compound are obtained for the processes $M^{2+} + Br^- + Me_6tren = [M(Me_6tren)Br]^+$ and $M^{2+} + 2Br^- + Me_5dien = M(Me_5dien)Br_2$ both in the gaesous state (bond dissociation enthalpies) and in aqueous solution. The results are discussed in terms of crystal field stabilization energies of the five-coordinated species and of the aquo ions. The stability of these five-coordinated complexes in aqueous solution increases in the order: $Mn < Fe \approx Ni < Co < Zn < Cu$. The enthalpy changes for the reaction of formation: $MBr_2(s) + ligand(l) = MBr_2 \cdot ligand(s)$ are also obtained. For both series the order of increasing heat evolved is: $Mn < (Fe, Ni) < (Co, Cu, Zn)$. Throughout, a comparison is made with complexes of octahedral and tetrahedral stereochemistry.

Introduction

Complexes of the bivalent ions of the first transition series with a coordination number of five are relatively little known in comparison with those having a coordination number of four or six. Recently renewed interest has been devoted to this type of complex, and a number of five-coordinated complexes of $3d^{5-10}$ metals have been prepared.[1-3]

The present calorimetric study investigates the tendency of the bivalent transition metal ions from manganese to zinc to form five-coordinated complexes

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[1] L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964), and previous references therein; L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965); L. Sacconi, P. Nanelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); G. S. Benner, W. E. Hatfield, and D. W. Meek, *ibid.*, **3**, 1544 (1964); J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, **207**, 72 (1965). For updated references see also L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

[2] (a) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (b) M. Ciampolini and N. Nardi, *ibid.*, **5**, 1150 (1966).

[3] M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).

with a given set of ligands. For this purpose we have chosen the complexes [M(Me$_6$tren)Br]Br[2] and M(Me$_5$dien)Br$_2$,[3] where Me$_6$tren is $N[CH_2CH_2N(CH_3)_2]_3$ and Me$_5$dien is $CH_3N[CH_2CH_2N(CH_3)_2]_2$. The reasons for this choice are (a) both types of complex form complete and isomorphous series and (b) the spin multiplicity of the complexes is the same as that of the corresponding free ions and the aquo ions. The [M(Me$_6$tren)Br]Br complexes have a trigonal-bipyramidal configuration with a bromine coordinated on a C_3 axis,[2] and the M(Me$_5$dien)Br$_2$ complexes have a configuration intermediate between that of a trigonal bipyramid and that of a square pyramid.[3,4]

The thermochemical data obtained from this work will be discussed in terms of the formation of (1) gaseous complexes from gaseous reagents, (2) solid complexes from reagents in a condensed phase, and (3) solid complexes from reagents in aqueous solution. In the first process, attention is focused on the strength of the coordinate links by excluding energetic terms due to lattice forces and solvation. The second process is concerned with the possibility of isolating the solid complexes. The third process allows us to obtain information about the relative stability of the five-coordinated species, which are rather unstable in aqueous solution.

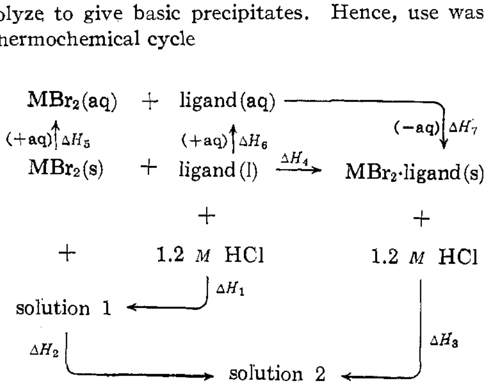
The results obtained for these five-coordinated complexes are compared with analogous data for complexes of different stereochemistry, with coordinated nitrogen or bromine. Thermochemical data suitable for this comparison are those for the series of octahedral compexes [M(en)$_3$]X$_2$[5] and [M(NH$_3$)$_6$]X$_2$[6,7] and for the series of tetrahedral complexes [(C$_2$H$_5$)$_4$N]$_2$[MBr$_4$],[8] where M is a metal in the series Mn to Zn.

Experimental Section

Materials.—The amines Me$_6$tren and Me$_5$dien and their metal complexes were prepared as described previously.[2,3] The anhydrous bromides were also prepared as already described.[8]

Calorimetric Measurements.—The calorimeter has already been described elsewhere.[9] The ampoule contained a weighed amount of the liquid amine, the complex compound, or the anhydrous bromide. The dewar flask contained a weighed amount of water, acid, or an acid solution of the amine. The acid was 1.22 *M* hydrochloric acid. The solid dissolved completely within 1–3 min of opening the bottle. The salt:water ratio was 1:2000 for ΔH_5 and 1:3000 for ΔH_3 (see below, cycle 1).

Procedure.—The heats of solution in water of the complexes investigated could not be measured directly, since many of them hydrolyze to give basic precipitates. Hence, use was made of the thermochemical cycle



(1)

This gives the thermochemical equations

$$\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3 \qquad (2)$$

$$\Delta H_7 = \Delta H_4 - \Delta H_5 - \Delta H_6 \qquad (3)$$

The heat of formation of the solid complexes, starting from the reagents in aqueous solution, ΔH_7 (namely $-\Delta H$ solution) is obtained from the combination of five terms.

The ΔH_2 value for [M(Me$_6$tren)Br]Br was taken equal to the measured ΔH_2 for M(Me$_5$dien)Br$_2$.

A couple of representative runs valid for the system Mn(Me$_5$dien)Br$_2$ are reported here. In the calorimetric ampoule the quantities were (in millimoles): Me$_5$dien, 3.193, 3.069; MnBr$_2$, 3.402, 3.455; Mn(Me$_5$dien)Br$_2$, 3.104, 3.098; Me$_5$dien, 4.670, 4.726. The corresponding quantities of liquids, present in the dewar flask, were (in grams): HCl, 172.5, 165.9; solution 1 (see cycle 1), 183.9, 186.7; HCl, 167.0, 166.5; H$_2$O, 168.3, 170.3. The heats evolved were, respectively (in calories): 119.3, 114.5; 55.98, 56.56; 77.76, 77.36; 79.48, 80.53.[10]

Results

Tables I and II contain the calorimetric data for the thermochemical cycle, described in the previous section, in the case of the Me$_6$tren and Me$_5$dien complexes, respectively. The heats of solution in water of the metal bromides (column 1, Table I) are larger than those in acid (column 2, Table I). The difference in the case of the bromides from manganese to copper lies between 1 and 2 kcal/mole and can be attributed mainly to a salt effect. For ZnBr$_2$ the difference is 3.63 kcal/mole, probably because of the endothermic effect arising from the formation of chloro complexes in the hydrochloric acid solution.[11]

The uncertainties in the values of ΔH_7 vary from ±0.08 to ±0.24 kcal/mole. These uncertainties include contributions due to the constant terms ΔH_1 and ΔH_6. The relative values of ΔH_7, therefore, are known to within an accuracy better than that shown in Tables I and II.

Discussion

Relative Bond Dissociation Enthalpies (BDE).—In this section we shall consider the process of dissociation of the complex ions, into metal ions and ligands, all being in the gaseous state. In the thermochemical cycle

$$\begin{tikzcd}
MBr_2(s) \arrow[d, "\Delta H_l(\text{salt})"] & + & \text{ligand}(l) \arrow[r, "\Delta H_4"] \arrow[d, "\Delta H^V"] & MBr_2\cdot\text{ligand}(s) \arrow[d, "\Delta H_l(\text{cpx})"] \\
M^{2+}(g) + 2Br^-(g) & + & \text{ligand}(g) & MBr_2\cdot\text{ligand}(g) \arrow[l, "D"']
\end{tikzcd} \qquad (4)$$

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[4] P. L. Orioli and M. Di Vaira, *Chem. Commun.*, 590 (1965).

[5] F. D. Rossini, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

[6] F. A. Cotton, *Acta Chem. Scand.*, **10**, 1520 (1956).

[7] K. B. Yatsimirskii, "Thermochemie von Komplexverbindungen," Akademie-Verlag, Berlin, 1956, p 92.

[8] P. Paoletti, *Trans. Faraday Soc.*, **61**, 219 (1965).

[9] P. Paoletti, R. Usenza, and A. Vacca, *Ric. Sci.*, **35**, 201 (1965).

[10] The data relating to all calorimetric runs have been deposited as Document No. 9122 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540 A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[11] L. G. Sillén and A. E. Martell in "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, p 289.

Table I

Calorimetric Results for $[M(Me_6tren)Br]Br$ Complexes[a]

	ΔH_5[b]	ΔH_2	ΔH_3	ΔH_4	ΔH_7
Mn	-18.15 ± 0.08	-16.41 ± 0.04	-31.19 ± 0.03	-33.51 ± 0.11	6.81 ± 0.22
Fe	-20.16 ± 0.06	-18.94 ± 0.04	-27.43 ± 0.05	-39.80 ± 0.13	2.53 ± 0.22
Co	-20.02 ± 0.07	-18.48 ± 0.03	-21.43 ± 0.07	-45.34 ± 0.14	-3.15 ± 0.24
Ni	-19.62 ± 0.04	-18.31 ± 0.04	-26.15 ± 0.06	-40.45 ± 0.14	1.34 ± 0.21
Cu	-8.85 ± 0.00	-6.78 ± 0.01	-10.51 ± 0.08	-44.56 ± 0.13	-13.54 ± 0.16
Zn	-16.65 ± 0.01	-13.02 ± 0.03	-15.93 ± 0.04	-45.38 ± 0.11	-6.56 ± 0.15

$\Delta H_1 = -48.29 \pm 0.04$ kcal/mole
$\Delta H_6 = -22.17 \pm 0.03$ kcal/mole

[a] All of these values are the mean of two determinations, and the units for all are kilocalories per mole. [b] Values taken from ref 8. For Mn and Fe the values in ref 8 contain a misprint: P. Paoletti, *Trans. Faraday Soc.*, **62**, 519 (1966).

Table II

Calorimetric Results for $M(Me_5dien)Br_2$ Complexes[a]

M	ΔH_8	ΔH_4	ΔH_7
Mn	-25.01 ± 0.04	-28.74 ± 0.11	6.44 ± 0.20
Fe	-24.50 ± 0.03	-31.78 ± 0.10	5.41 ± 0.17
Co	-21.57 ± 0.05	-34.25 ± 0.11	2.80 ± 0.19
Ni	-23.73 ± 0.03	-31.92 ± 0.10	4.73 ± 0.15
Cu	-7.99 ± 0.03	-36.13 ± 0.07	-10.25 ± 0.08
Zn	-13.47 ± 0.06	-36.89 ± 0.12	-3.21 ± 0.14

$\Delta H_1 = -37.34 \pm 0.03$ kcal/mole
$\Delta H_6 = -17.03 \pm 0.01$ kcal/mole

[a] All of these values are the mean of two determinations, and all units are kilocalories per mole.

Table III

Bond Dissociation Enthalpies Relative to That of the Manganese Compounds

Metal	D(metal) − D(manganese), kcal/mole	
	$[M(Me_6tren)Br]^+$	$M(Me_5dien)Br_2$
Fe	28	25
Co	53	46
Ni	66	63
Cu	81	80
Zn	62	58

when ligand = Me_6tren, the system $MBr_2 \cdot$ligand (g) consists of the free gaseous ions $[M(Me_6tren)Br]^+$ and Br^-, whereas when ligand = Me_5dien, the system $MBr_2 \cdot$ligand(g) is formed by the gaseous molecules $M(Me_5dien)Br_2$. D is the enthalpy of bond dissociation for the gaseous complex. The significance of the other symbols is clear from the text. The following equation is obtained from this cycle

$$D = \Delta H_1(\text{salt}) + \Delta H^V - \Delta H_1(\text{cpx}) - \Delta H_4 \qquad (5)$$

The values of ΔH_4 are shown in Tables I and II, and the values of ΔH_1(salt) are taken from ref 8. Assuming that isomorphous complexes have the same lattice energy (and hence lattice enthalpy ΔH_1),[12,13] it is possible to calculate the difference D(metal) − D(manganese) for each of these series (Table III). These differences are plotted in Figure 1 against the atomic number of the metal. The two curves are nearly parallel although the complexes $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$ have different sets of donor atoms, N_4Br and N_3Br_2, respectively. The values increase steadily from manganese to copper, while that of zinc is slightly less than the value of nickel.

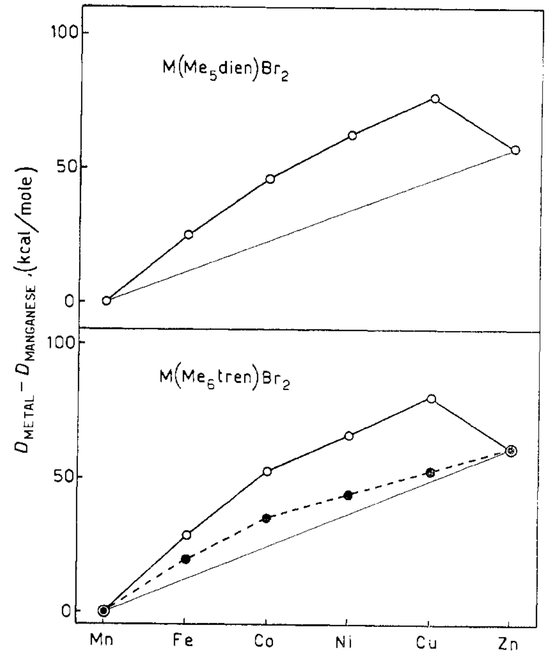

Figure 1.—Relative bond dissociation enthalpies of the compounds $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$ in the gaseous state: ○, experimental values; ●, values corrected for CFSE.

As is well known, the shape of the BDE curve has been successfully interpreted in terms of crystal-field stabilization energies (CFSE) for various octahedral[14] and tetrahedral[8,13] complexes. An analogous interpretation can be used for the BDE curve of five-coordinated complexes. Two approaches are possible. In the first the optical CFSE values are calculated for the compounds $[M(Me_6tren)Br]Br$, which have a more regular geometry, by fitting their spectra to the appropriate energy level diagram for trigonal-bipyramidal complexes.[15–17] These values, which admittedly imply various assumptions about the necessary parameters

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(12) Blake and Cotton[13] estimate that the spreading of the lattice energie^{S} for the isomorphous complexes of the series $[(C_6H_5)_3AsCH_3]_2[MCl_4]$, where M is one of the metals in the series Mn to Zn, is about 1.6 kcal/mole. Using a similar procedure we estimate that the spreading of the lattice energies of the complexes $[M(Me_6tren)Br]Br$ is about 1.8 kcal/mole. These compounds have a cubic lattice of the distorted sodium chloride type (Drs. Di Vaira and Orioli, private communication). From X-ray powder photographs we have calculated the following edges for the cubic unit cells (in Angstroms): Mn, 12.34; Fe, 12.29; Co, 12.13; Ni, 12.09; Cu, 12.14; Zn, 12.19. The relevant data are available through the ASTM X-ray powder diffraction file. For the molecular solids $M(Me_5dien)Br_2$, the differences in lattice energies are presumably even smaller.

(13) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3**, 5 (1964).

(14) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).

(15) Such diagrams have been obtained by using the procedure and parameters of ref 3b, where the case of iron(II) is considered. For cobalt(II) and nickel(II), see also ref 16 and 17, respectively.

(16) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966).

(17) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

(in kilocalories per mole), are: Fe, 9; Co, 17; Ni, 22; Cu, 28. Figure 1 shows that the BDE, corrected with these CFSE values, of the compounds $[M(Me_6tren)Br]Br$ increase steadily from manganese to zinc in accordance with the request of crystal-field theory.

A second approach can be made in terms of the *ratios* between the CFSE values of the high-spin configurations d^6–d^9 assuming a crystal-field of fixed geometry and strength. For high-spin trigonal-bipyramidal complexes the CFSE ratios for Fe, Co, Ni, and Cu are 1:2.0:2.3:2.6, respectively.[18] For a square-pyramidal stereochemistry, to which the complexes $M(Me_5dien)Br_2$ tend, the ratios are 1:2.0:2.2:2.0.[18] Now the differences between the experimental BDE values and those calculated by the usual interpolation (see Figure 1) are for $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$ (in kilocalories per mole), respectively: Fe, 16, 14; Co, 28, 23; Ni, 29, 28; Cu, 31, 30. The ratios between these values are thus 1:1.8:1.8:1.9 for the Me_6tren complexes and 1:1.6:2.0:2.1 for the Me_5dien complexes. The agreement between the expected ratios and the ratios actually found is satisfactory considering the uncertainties in the experimental values, the limitations of the concept of linear interpolation, and the other assumptions made.

The differences between the BDE values for manganese and zinc complexes, termed "transition series contraction energy" by George[19] for several series of complexes with different ligands and different stereochemistry (in kilocalories per mole) are: $[M(Me_6tren)Br]^+$, 62; $M(Me_5dien)Br_2$, 58; $[MI_4]^{2-}$, 59;[20] $[MBr_4]^{2-}$, 57;[8] $[MCl_4]^{2-}$, 54;[21] $[M(NH_3)_6]^{2+}$, 49,[6] 52;[7] $[M(H_2O)_6]^{2+}$, 47 [22] kcal/mole. The data reported here are consistent with the suggestion of Gill and Nyholm[23] that the contraction energy was proportional to the polarizability of the ligands.

Formation of Complexes in Condensed Phases.—Let us consider the processes

$$MBr_2(s) + Me_6tren(l) \longrightarrow [M(Me_6tren)Br]Br(s) \quad (4a)$$

$$MBr_2(s) + Me_5dien(l) \longrightarrow M(Me_5dien)Br_2(s) \quad (4b)$$

The enthalpy changes for processes 4a and 4b are listed in the penultimate columns of Tables I and II, respectively. The reactions are all strongly exothermic, and, for a given element, the heat evolved is greater by 5–11 kcal/mole for the Me_6tren complexes than the the Me_5dien complexes. These heats decrease for both series of compounds in the order: (Zn, Cu, Co) > (Fe, Ni) > Mn, which differs somewhat from the order of BDE values. The most marked difference occurs for nickel and copper for which the formation of five-coordinated complexes appears to be less favored than in the gas phase. In fact, the sequence of ΔH_4 values is determined by the differences between the BDE values of the complexes and the lattice energies of the metal bromides (*cf.* eq 5). These bromides are octahedral polymers,[24] and for $NiBr_2$ and $CuBr_2$ this configuration in the solid state seems to be favored relative to the five-coordinated one.

It is interesting to compare the enthalpy changes for reactions 4a and 4b, respectively, −33.5 to −45.4 and −28.7 to −36.9 kcal/mole for Mn to Zn, with those of the reactions

$$MBr_2(s) + 2[(C_2H_5)_4N]Br(s) \longrightarrow [(C_2H_5)_4N]_2[MBr_4](s) \quad (4c)$$

−17 to −1 kcal/mole for Mn to Zn,[8] and

$$MBr_2(s) + 3en(l) \longrightarrow [M(en)_3]Br_2(s) \quad (4d)$$

−71, −71, and −60 kcal/mole for Co, Ni, and Zn,[5] respectively. It is not surprising that the heats evolved in the formation of octahedral complexes, known for a long time and considered to be very stable, are much greater than those evolved in the formation of five-coordinated and tetrahedral complexes. In fact, it is improbable that in processes 4a–4d the entropy changes would have such large negative values as to make the sequence of the free energy changes appreciably different from that of the enthalpy changes.

Formation of Complexes in Aqueous Solution.—Let us consider the process

$$MBr_2(aq) + ligand(aq) \longrightarrow MBr_2 \cdot ligand(s) \qquad \Delta H_7$$

(*cf.* cycle 1) which concerns the formation of solid complexes $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$ from the appropriate salts and ligands in aqueous solution. It is convenient to distinguish two stages in this process: (a) removal of the six molecules of water from the primary coordination sphere of the aquo ion and formation of the five-coordinated complex and (b) precipitation of the complex formed. It seems probable that the enthalpy changes for process b would be essentially the same for each of these series of isomorphous compounds, since the metal ion is very effectively shielded by the ligands. Thus the order of the ΔH_7 values can be taken to be the same as the order of the enthalpy changes for the formation of the five-coordinated complexes from the appropriate aquo ions in aqueous solution (process a). The values of ΔH_7 for $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$ are shown graphically in Figure 2 (curves A and B) where the values for manganese compounds are taken conventionally equal to zero. The two curves are similar and the values increase in the order: Mn < Fe ≈ Ni < Co < Zn < Cu. This sequence can be compared with that for the formation of the tetrahedral complexes MBr_4^{2-} [8] (Figure 2, curve C, $\Delta H_{Mn} = 0$) and MCl_4^{2-},[13,21] *i.e.*, Ni ≪ Fe < Co < Mn < Cu < Zn.[25] For octahedral complexes the well-known "natural order of stability,"[26] which is determined by the

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[18] C. J. Ballhausen and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd.*, **29**, 14 (1955); *cf.* F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 55.

[19] P. George, *Rec. Trav. Chim.*, **75**, 671 (1956); *cf.* also ref 14, p 430.

[20] P. Paoletti, A. Sabatini, and A. Vacca, *Trans. Faraday Soc.*, **61**, 2417 (1965).

[21] P. Paoletti and A. Vacca, *ibid.*, **60**, 50 (1964).

[22] *Cf.* ref 14, p 416.

[23] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[24] *Cf.* A. F. Wells, in "Structural Inorganic Chemistry," Oxford University Press, London, 1962, pp 345, 346.

[25] In the case of the MCl_4^{2-} ions this order has been satisfactorily explained in terms of the difference in CFSE between the tetrahedral species and the corresponding octahedral aquo ions.[13]

[26] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

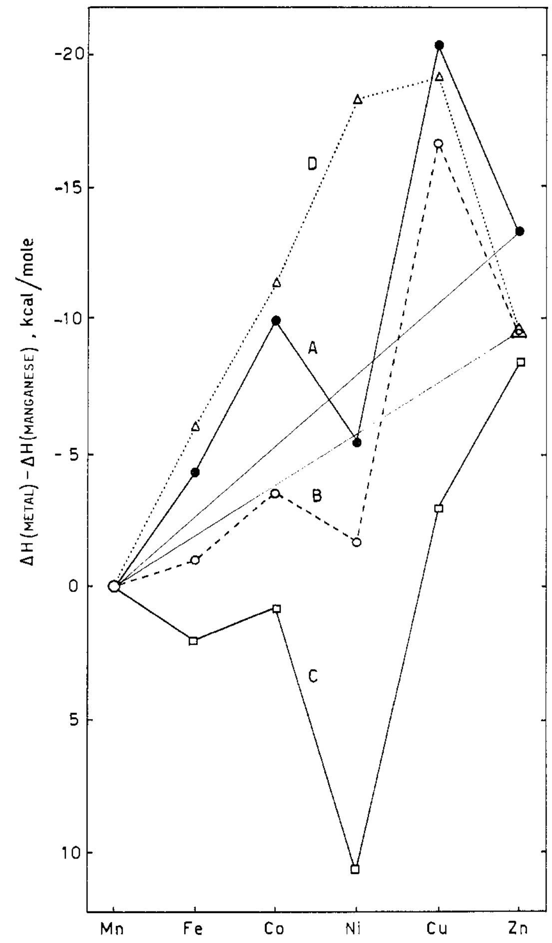

Figure 2.—Relative values of the enthalpy changes for the formation of complex compounds from aquo ions: A, $[M(Me_6tren)Br]^+$; B, $M(Me_5dien)Br_2$; C, $[MBr_4]^{2-}$; D, $[M(dien)_2]^{2+}$.

enthalpy order, is usually valid. As an example valid for octahedral complexes, curve D of Figure 2 shows the enthalpy changes, relative to that of manganese, for the reaction

$$M^{2+}(aq) + 2(dien(aq)) = [M(dien)_2]^{2+}(aq)$$

(dien = $HN[CH_2CH_2NH_2]_2$). In this case, the high stability of the $M(dien)_2^{2+}$ species in aqueous solution allowed direct measurements of the heat effect for the above reaction.[27]

For the five-coordinated species there are two characteristics of the sequence of ΔH_7 values which deserve comment. Firstly, the ΔH_7 values are more negative for the complexes of zinc than for those of manganese. This can be explained in terms of the same electronic factors which are responsible for the different "transition series contraction energies" of the five-coordinated complexes and of the aquo ions. Steric effects can also play a role because of the different size of the manganese(II) and zinc(II) ions.[19] Secondly, relative to the straight line Mn–Zn, the most positive experimental ΔH_7 values are those for nickel while the most negative values are those for copper. This can be attributed, at least in part, to differences between the CFSE of the five-coordinated complexes and those of the octahedral aquo ions. These are expected to favor the formation of the five-coordinated complex in the case of copper but the formation of the aquo ion in the case of nickel. Actually, the differences between the experimental values and the interpolated values of ΔH_7 are, for $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$, respectively (in kilocalories per mole): Fe, 2.0, −1.0; Co, 4.5, 0.0; Ni, −2.5, −4.0; Cu, 9.5, 9.0. The differences in optical CFSE values of the aquo ions[13] and of the $[M(Me_6tren)Br]^+$ ions (in kilocalories per mole) are: Fe, 0; Co, 0; Ni, −7; Cu, 9. The agreement can be considered satisfactory in view of the uncertainties in the CFSE values both for the five-coordinated species and for the aquo ions, as compared with the small differences in the ΔH_7 values.

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